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14. ABSTRACT In this study, two processes are investigated and compared for producing nano-scale energetic oxidizer particles. Rapid Expansion of a Supercritical Solution (RESS) was investigated and a similar process called the Rapid Expansion of a Supercritical Solution into an Aqueous Solution (RESS-AS) was investigated as well. Both processes were used to precipitate particles of RDX and bis (2,2,2-trinitroethyl)-3,6-diaminotetrazine (BTAT). Under similar pre-expansion conditions, the RESS process produced RDX particles around 100 nm in diameter and the RESS-AS process produced particles around 30 nm. Permanent agglomeration was prevented by coating the RDX particles with polyvinylpyrrolidone (PVP) and polyethylenimine (PEI). BTAT particles produced from the RESS process were around 100 nm in diameter and agglomerated while the RESS-AS process produced nano-sized square rods. The decomposition exotherm from TGA/DSC testing of RDX particles produced from the RESS-AS process was 25 K lower than micron-sized RDX and RESS synthesized RDX.					
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Synthesis of Energetic Materials by Rapid Expansion of a Supercritical Solution into Aqueous Solution (RESS-AS) Process

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ABSTRACT

Energetic crystalline nanoparticles have many benefits when incorporated into a propellant or explosive. They have been shown to be less sensitive to impact and can also change the energetic performance of a propellant or explosive. In this study, two processes are investigated and compared for producing nano-scale energetic oxidizer particles. Rapid Expansion of a Supercritical Solution (RESS) was investigated and a similar process called the Rapid Expansion of a Supercritical Solution into an Aqueous Solution (RESS-AS) process was used to produce RDX and bis(2,2,2-trinitroethyl)-3,6-diaminotetrazine (BTAT) particles. For similar pre-expansion conditions, the RESS process produced RDX particles with an average size of approximately 100 nm and the RESS-AS process produced RDX particles with an average size of 30 nm. The small RDX particles were able to be coated and stabilized from permanent agglomeration in the RESS-AS process with polyvinylpyrrolidone (PVP) and polyethylenimine (PEI). The energetic material BTAT was produced initially in Germany and reprocessed first by the RESS process and nearly spherical particles of around 100 nm were created that were agglomerated. Later, BTAT particles were produced by the RESS-AS process by expanding into an aqueous solution of SDS and water produced small nano-sized rods (width and height around 100 nm) without agglomeration. The synthesized RDX particles were tested in a TGA/DSC and it was found that RESS synthesized RDX experienced nearly no temperature shift in its melting and decomposition temperature in comparison to larger micron-sized RDX. However, the RESS-AS synthesized RDX particles experience a decomposition exotherm about 25° C below the value for conventional RDX. The lowered melting point suggests that RESS-AS synthesized RDX particles have different thermodynamic properties that should be investigated further. One of these properties associated with the nano-sized particles is the ability of storing extra energy on their surface and/or due the high percentage of surface molecules with lower coordination numbers.

INTRODUCTION

Energetic materials are commonly used as additives in explosive and propellant formulations. An attractive energetic material provides a high amount of energy release while being relatively insensitive to accidental initiation. However, there is usually a delicate balance between the two as energetic materials that release more energy or perform better are often more sensitive to initiation. Because of this, a way to reduce the sensitivity and still increase the performance of an energetic material would be attractive.

It is important to decrease the sensitivity of an energetic material to impact, shock, friction, and electrostatic discharge (ESD). Reducing the risk of accidental ignition of the energetic ingredients is also

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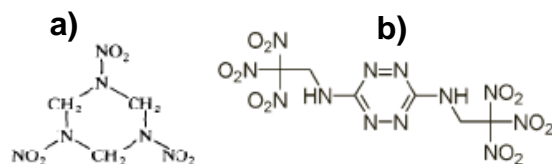
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important for raw energetic material handling and transport as well during the mixing and production stages of explosives, propellants, or solid fuels. The size and shape of crystalline particles, particle size distribution, impurities, and any defects in individual crystals all affect the sensitivity of energetic materials. It has been shown for RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine) and other energetic materials that as the average particle size is decreased, sensitivity to impact decreases as well.^{1,2} It was proposed that this decrease in impact sensitivity comes from a reduction of imperfections or dislocations in a crystal. Also, particles with a spherical shape are less sensitive to initiation as well.^{3,4} Not only are spherical particles a more optimal shape for sensitivity reasons, they are also more ideal for propellant/explosive processing applications in comparison to needle-like particles.⁵ In order to create a high-density, packing-defect free solid propellant, the particle size, morphology, and size distribution must all be controlled.

In addition to insensitive energetic materials, synthesizing energetic oxidizer particles on the nano-scale could also be advantageous for performance reasons. If nano-sized oxidizers were intimately mixed with nano-sized metallic fuels, the diffusion times between fuel and oxidizer could be greatly enhanced. Also, nano-scale particles have been known to have different thermodynamic properties in comparison to larger particles. As the surface-area-to-volume ratio (S/V) of a particle increases, thermal properties such as the melting temperature and heat capacity decrease.⁶ Also, nanoparticles carry extra energy on their surface as a result of “dangling bonds”. These lower coordination number molecules are not exclusive to nanoparticles, but they make up a noticeable percentage of a particle's mass if it has a high S/V ratio. The lower coordination number causes the bond lengths of molecules to be shorter by the surface than they otherwise would be in the center of the particle. This could allow more energy to be released during combustion of the particles and is sometimes referred to as storing energy at the surface. In addition, a study by Pivkina *et al.* has shown that nano-sized RDX and ammonium nitrate powders when pressed into pellets burned significantly faster at elevated pressures.⁷ This was assumed to be from the enhanced surface area of the nanoparticles which allowed for greater heat transfer of hot products diffusing onto their surfaces.

This investigation studies two energetic materials: RDX and another energetic material called bis(2,2,2-trinitroethyl)-3,6-diaminotetrazine (BTAT). The molecules of RDX and BTAT are shown in Figure 1. RDX was chosen because a large amount of information is known about it and enhancements in performance and sensitivity could be appreciated because of its wide use. BTAT shows higher detonation velocities and better oxygen balances than RDX and HMX (Table 1).^{8,9} However, this material has a slightly higher sensitivity than RDX, probably resulting from a less than ideal morphology.

Nanoparticles were created by the Rapid Expansion of a Supercritical Solution (RESS) process in which a solution of supercritical fluid and solute is mechanically expanded into an ambient environment. Another similar process was also used called the Rapid Expansion of a Supercritical Solution into an Aqueous Solution (RESS-AS) process in which a supercritical fluid containing dissolved solute is expanded into an aqueous solution of dispersant and water. Both were investigated to compare how the size and shape of these two materials can be controlled through these two different processes. The overall goal of this study was to produce nano-sized and nearly spherical energetic particles with both the RESS and RESS-AS processes. In addition, adequate dispersants have been selected and used to observe the effect of different dispersants on the final output of the synthesized particles. In addition, thermal properties of the produced particles have been examined to see if there are differences between the original bulk-sized energetic materials and the nano-sized particles.



**Figure 1. High performance energetic materials considered for supercritical precipitation; a) RDX
b) BTAT**

**Table 1. Molecular and performance parameters of energetic materials considered
(from Göbel and Klapötke⁸)**

Energetic Material	Molecular Formula	Density (g/cc)	Detonation Velocity (m/s)	Impact Sensitivity (J)
RDX	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$	1.82	8750	7.4
BTAT	$\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}$	1.886	9261	7

BACKGROUND

Traditionally, the size and shape of energetic particles are altered through liquid solvent precipitation or by mechanical means such as milling or grinding a larger material. Liquid solvent precipitation often leads to particles that have a wide size distribution from non-uniform degree of supersaturation. Additionally, particles smaller than the micron size scale cannot be formed and the produced particles often have solvent inclusions in them from the solvent not diffusing out of the growing particle effectively. Mechanical milling can be dangerous as kinetic energy is used to grind and break the particles apart. This can cause accidental initiation of the particles. Also, precise control over the size or shape of the particles is difficult to predict using milling. In addition, it is difficult to mill a material less than around a micrometer using standard milling techniques. An alternative method of processing energetic materials is through homogeneous nucleation of the dissolved solute in a supercritical fluid during its expansion process. Supercritical fluids have unique advantages as a solvent; they experience a large change in density around their critical point when pressure or temperature is varied and they have gas-like transport properties. The large change in density of supercritical fluids allow for a large degree of supersaturation if they are used as a solvent and mechanically expanded. The gas-like transport properties allow for high diffusivities and fast mechanical perturbations leading to uniformly sized particles that do not possess solvent inclusions. Supercritical fluid precipitation has been used to precipitate solid particles of significantly smaller size and different morphology than in conventional liquid solvent precipitation.¹⁰ Both of these attractive features are ideal for energetic oxidizers because the size and shape of the particles strongly affects their sensitivity.

The RESS process has been used in many industrial fields such as the polymer and pharmaceutical industry.¹¹ Initial research involving energetic materials and the RESS process was investigated by Teipel *et al.*¹² in which they synthesized the energetic material TNT. More recently, Stepanov *et al.*¹³ used the RESS process to synthesize particles of RDX. Particles approximately 110 ± 35 nm in diameter were produced, showing dramatic reductions in impact sensitivity. The thermal properties of the particles were tested and were found to be similar to larger RDX particles. However, at 110 nm only a small percentage of the particle's mass is located at the surface of the particle and any alterations in thermal properties should not be expected.

While the RESS process has been successful at producing fine and uniform particles, particles have been larger than what calculations have predicted from nucleation and growth by precipitation. It seems that the extra growth from the RESS process comes from particle coagulation in the free jet after the nozzle exit since the mechanical expansions are often highly under-expanded.¹⁴ The coagulation results in particles that are bridged together, are larger than expected, and show significant agglomeration and aggregation from the coagulation process. Also, only limited control over the final particle shape is possible with the RESS process. This is because only pre-expansion conditions can be modified, rather than post-expansion conditions, as the expansion environment can affect the free energy

of a precipitating surface. It has been proposed by researchers that the RESS process could be optimized by expanding the supercritical solution into a stabilizing liquid solution often made of water and dispersant.¹⁵ The dispersant adsorbs or bonds to the particle surface in the aqueous solution to limit the growth of the particles by condensation and coagulation. The adsorbed dispersant also stabilizes the particles in solution, preventing them from permanently agglomerating. The process is called the rapid expansion of a supercritical solution into an aqueous solution (RESS-AS). A graphical representation of the RESS-AS process is shown in Figure 2. It has been used by many researchers outside the energetic materials field to produce submicron particles from materials that could only be produced at micron size from the RESS process.^{16,17,18} The process has yet to be used in the energetic material community and could be useful in making small nano-sized particles significantly smaller than the RESS process does. Not only has the RESS-AS process been shown to reduce the size of particles even further than the RESS process, it has also shown that it can prevent agglomeration and change the shape of particles. Nothing in the RESS process prevents van der Waals forces from causing the newly synthesized particles to agglomerate and aggregate. However, the RESS-AS process provides a dense fluid to provide electrostatic repulsion. In addition, if dispersants are adsorbed to the particle's surface, steric repulsion can be achieved. Steric repulsion involves the adsorption or chemisorption of molecules to the surface of the particle. If the molecules are long enough (e.g. polymers) then the coated particles can be prevented from coming close enough to permanently agglomerate through the physical interference of these adsorbed molecules. From the positive results experienced in other industries, the process could be highly useful for processing energetic materials into an ideal size and shape. The RESS-AS process is also useful in that the surfaces of the precipitated particles can be chemically altered in solution for desirable effects such as making the particles more compatible with other materials and changing the surface reactivity of the material itself. These benefits are important, because nanoparticles need to be handled in the suitable environment to avoid undesirable problems such as coagulation and aggregation which mitigate the benefits that come with their small size. Having small particles in suspension allows them to be processed into propellants and explosives in novel ways that will allow their true size to be utilized.

The RESS-AS process offers several benefits for manufacturing propellants and explosives. One benefit is that the process allows one to coat small nano-sized particles while they are still in a dispersed suspension. This allows one to make the particles more compatible with certain materials. Another benefit is that the small uniform particles could have a reduced sensitivity to impact or shock. One other benefit is that the nano-sized particles would have more stored energy than conventionally sized oxidizer particles because of their high S/V ratio. Burning rates of the particles could be enhanced as well from the high surface area. Furthermore, the particles could be mixed with nano-sized metal fuel particles to reduce the diffusion distance between fuel and oxidizer.

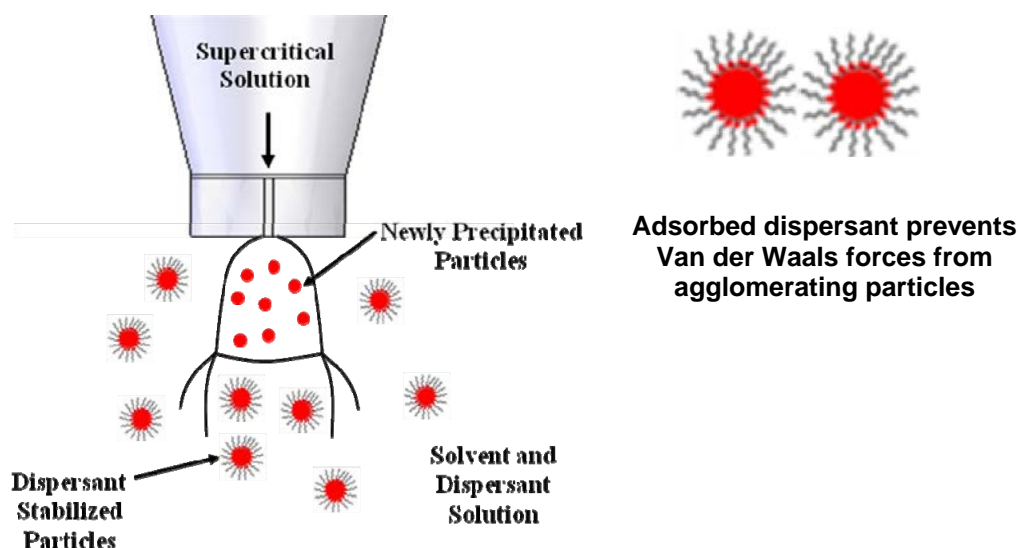


Figure 2. Representation of the RESS-AS process

EXPERIMENTAL WORK

SAMPLE PREPARATION

Military grade RDX was obtained from a supplier containing a non-negligible percentage of HMX (~5% by mass). The original crystals were Type II, Class I. Since the RDX crystals contain a fairly large weight percentage of HMX, purification through recrystallization was necessary. Through an acetone recrystallization process, the percentage of HMX was significantly reduced, increasing the percentage of RDX to nearly 100%. In this process, the as-received RDX was dissolved in high-purity acetone at elevated temperature and the solution temperature was then dropped to precipitate RDX, but not HMX. The recrystallized particles were then dissolved in acetone and used to coat glass beads to increase solute surface area which in turn decreases the dissolution time of the solute in the supercritical fluid.

BTAT particles were synthesized at Ludwig Maximilian University (LMU) of Munich and shipped to the Pennsylvania State University wetted with water for safety reasons. A field emission scanning electron microscope (FE-SEM) image of the BTAT particles can be seen in Figure 3 (b) along with the original RDX particles in Figure 3 (a). The as-received BTAT particles were plate like in morphology and many micrometers in length. The particle size and morphology are not suitable for sensitivity or processing purposes. Therefore, this material represents an ideal candidate for reprocessing through supercritical fluid precipitation. The impact sensitivity of the particles should be improved through reprocessing to smaller and better shaped particles. The received BTAT was dissolved in acetone and used to coat glass beads in a similar manner as RDX.

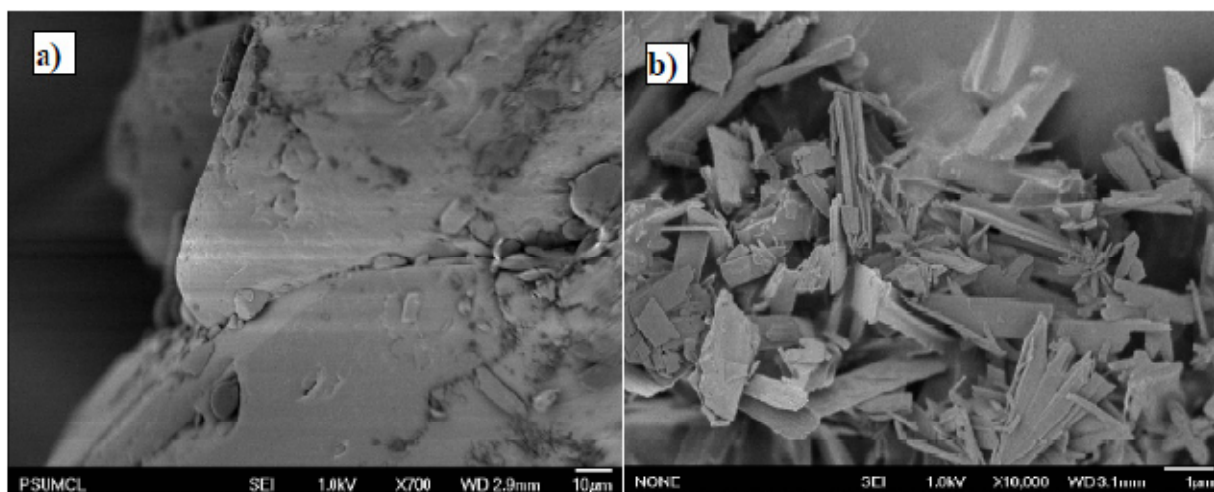


Figure 3. FE-SEM images of energetic materials used in the study before supercritical fluid processing a) Type II, Class I RDX b) BTAT

EXPERIMENTAL SETUP

The system process flow diagram is shown in Figure 4. The RESS and RESS-AS process are identical besides how the supercritical solution is expanded. The system is custom-designed and consists of a solvent manifold which delivers CO₂ to an industrial compressor (Hydropac; Fairview, Pennsylvania) which acts to pressurize the working fluid or solvent. The system also has a heat exchanger to ensure that all CO₂ delivered to the pump is a liquid for maximum pumping efficiency. The supercritical fluid is pumped into a temperature controlled saturation vessel containing solute-coated glass beads. The solute was then dissolved in a supercritical fluid to create a supercritical solution. The saturation vessel contains a Teflon coated silicon o-ring for sealing due to its resistance to solvents and

large operating temperature range. The saturation vessel was pressurized using a control program for the operation of the high-pressure compressor with a preset saturation vessel pressure. Similarly, the temperature of the solution in the saturation vessel was controlled by a feedback loop and thermostat control circuit to power a jacket heater surrounding the saturation vessel. After adequate time for dissolution, the supercritical solution was flown through the system and through a micro-orifice nozzle to be rapidly expanded. Before supercritical solution expansion, a bypass line is used to pressurize the downstream lines to ensure that steady state conditions are achieved for the entire test. The supercritical solution was then expanded into an expansion vessel.

The main difference between the RESS process and the RESS-AS process are their expansion vessels. With the RESS process, the supercritical solution is expanded into a gaseous (air) environment. In contrast, the supercritical solution is expanded into a water and dispersant solution for the RESS-AS process. An image of this expansion can be seen in Figure 5. For the RESS conditions, the expansion created dry ice which was later collected and allowed to sublime. This allowed for particles to be collected gravimetrically. For the RESS-AS conditions, the particles were entrained in the aqueous solution to create a colloidal suspension. The suspension ensured that the particles were kept in a well dispersed state. Particles are removed from solution by centrifuging, filtering, or vacuum boiling.

For the RESS-AS system, the nozzle assembly was placed an inch under the water and dispersant solution. Dispersants were mixed with ACS grade deionized water and care was taken to make sure the aqueous solutions were free from contaminants. The supercritical solution was then expanded into this environment. The water and dispersant solution volume was approximately 500 mL. The temperature of the solution was monitored with a K-type thermocouple. Heaters could control the temperature of the water to keep it at 25 ± 5 °C. Different amounts of dispersant and different types of dispersants were used. The pH value of the aqueous solution was measured before and after each test. Care had to be used to prevent the solution from leaving the expansion vessel due to excess foaming during the expansion process. To mitigate this problem, a N₂ purge was used to suppress the foam during a test. All tests were conducted with a pre-expansion pressure of 34.5 MPa, a pre-expansion temperature of 363 K, and an orifice nozzle diameter of 100 μ m. Tests were conducted for approximately 6 minutes. The resulting suspension was then placed in a container and stored. The supercritical solution was expanded into the aqueous solution multiple times to increase the amount of solid particles in the suspension. Typically 500 mg of particles were precipitated into 500 ml of aqueous solution. It is important to note that CO₂ readily dissolves in water and creates carbonic acid. This lowered the pH level of the aqueous solution to a value of 4.5. The experimental tests conducted are shown in Table 2.

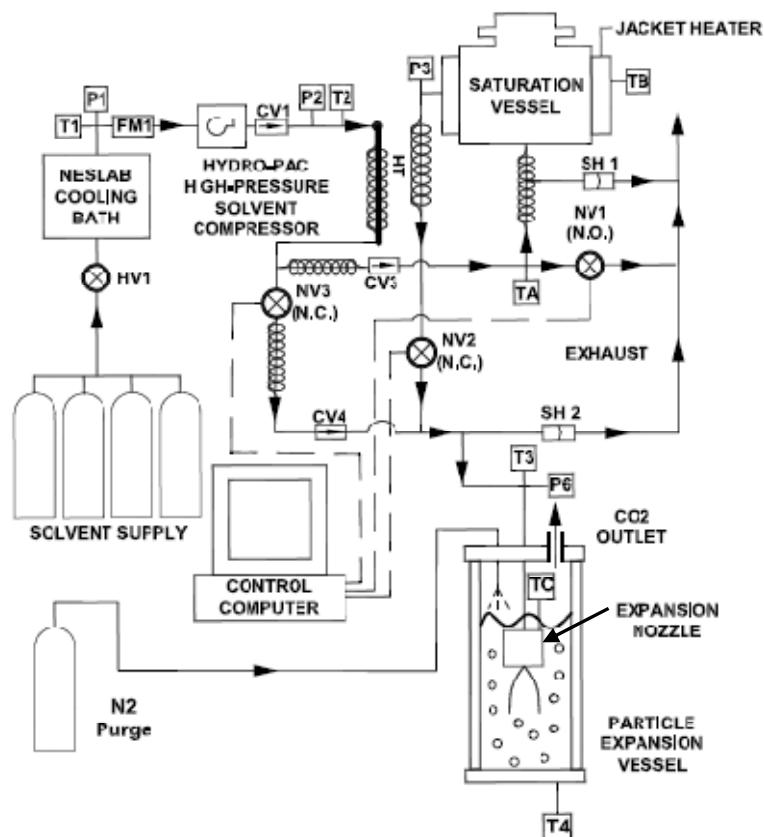


Figure 4. RESS-AS flow diagram

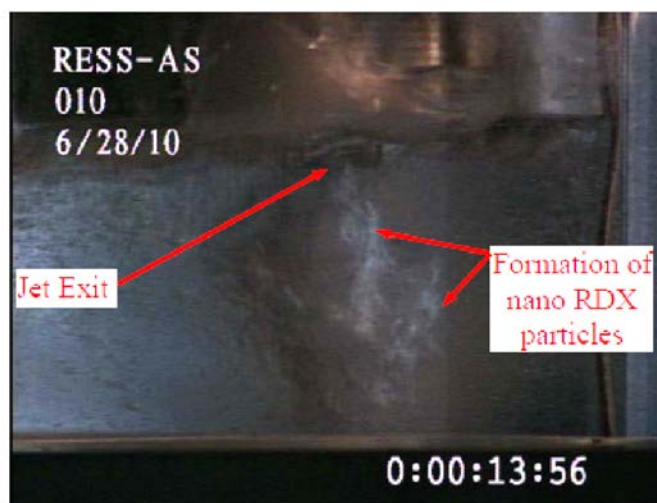


Figure 5. Supercritical solution expansion into water and NVP solution (Test 003)

Table 2. Tests conducted with RESS and RESS-AS processes

Test	Solute	P ₀ (MPa)	T ₀ (K)	D (μm)	Receiving Solution	Dispersant Wt %	Zeta Potential (mV)
001	RDX	34.5	363	100	None	None	N/A
002	RDX	34.5	363	100	Water	None	-29
003	RDX	34.5	363	100	Water and NVP	0.050	-10
004	RDX	34.5	363	100	Water and PVP	0.100	-12
005	RDX	34.5	363	100	Water and PVP	0.005	-9
006	RDX	34.5	363	100	Water and PEI	0.050	20
007	RDX	34.5	363	100	Water and PEI	0.005	20
008	BTAT	34.5	363	100	None	None	N/A
009	BTAT	34.5	363	100	Water	None	Not measured
010	BTAT	34.5	363	100	Water and SDS	0.005	Not measured

SELECTION OF DISPERSING AGENTS

Different types of dispersing agents were chosen to evaluate their effect on the particle morphology, size, and state of dispersion in the RESS-AS process. Making sure that fine particles are adequately dispersed and stable in an aqueous suspension requires balancing the forces from attractive van der Waals forces and repulsive electrostatic forces. Colloidal stability is achieved when the repulsive forces are stronger than the attractive forces.¹⁹ This is achieved by changing the charge at a particle's shear layer in solution. Also, steric methods can be used to stabilize particles in a liquid environment. Steric repulsion is achieved by coating the particle with a polymer or molecule that is long enough to prevent the particles from coming close enough to permanently agglomerate from van der Waals forces (see Figure 2). The adsorbed polymer has loops and tails that act to repel other particles in a steric manner.²⁰ This prevents the particles from coming in close enough contact to aggregate. The polymers can also be charged to provide electrostatic dispersion as well (cationic or anionic polymer).

The RESS-AS suspension had a pH level of approximately 4.5 from the dissolution of CO₂, creating carbonic acid during the expansion process. The zeta potential at this pH was determined to be -30 mV. Dispersing agents were chosen to coat the particles to prevent them from permanently agglomerating. Four molecules that were chosen to provide steric repulsion for the energetic particles are shown in Figure 6. Polyvinylpyrrolidone (PVP; Aldrich, Mw~55,000 g/mol) was chosen as a potential dispersant because it is soluble in water and is attracted to surfaces with a negative charge such as RDX in water. In comparison the monomer of PVP, 1-vinyl-2-pyrrolidone (NVP; Aldrich, Mw~111 g/mol) was also investigated to see if it would be a long enough molecule to provide steric hindrance to agglomeration. The potential benefits of NVP is that it is a smaller molecule and would coat the particles with less material. Sodium dodecyl sulfate (SDS; VWR, Mw~288 g/mol) was also used as a potential dispersant for BTAT. Finally, polyethylenimine (PEI; Aldrich Mw ~ 800 g/mol) was used because it was thought that it would have an affinity for the NO₂ groups on RDX and would provide cationic electrostatic dispersion along with steric dispersion from being a polymer. The polymers were chosen with different molecular weights because this would affect their radius of gyration which would alter the coating thickness on the particles. For performance reasons, it is desirable to coat the particles with as little material as possible and still keep them dispersed. The coating thickness from the polymers is directly proportional to the radius of gyration of the polymer in solution. The radius of gyration for a polymer can be expressed as:

$$R_g = \frac{1}{\sqrt{6}} \sqrt{\frac{M_w}{M_{w_0}}} l \quad (1)$$

where R_g is the radius of gyration for the polymer in solution, Mw is the molecular weight of the polymer, Mw_0 is the molecular weight of the monomer, and l is the contour length of the polymer. Therefore, the molecular weight of the polymer is important as if the polymer is not large enough it may not provide enough steric hindrance. From this equation, PVP would have the largest coating thickness and NVP the smallest. However, if the polymer is too large it will coat your particles with too much excess material.

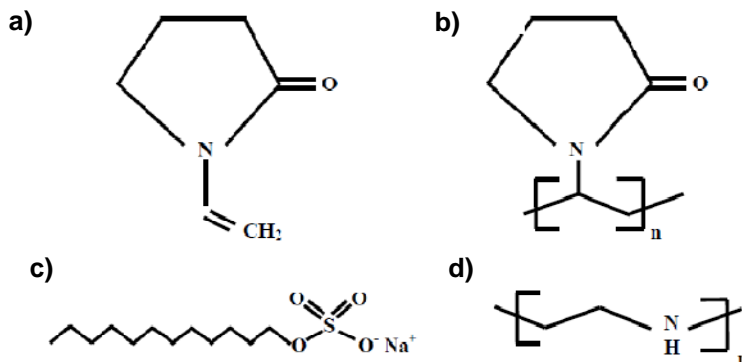


Figure 6. Adopted dispersing agents a) 1-Vinyl-2-pyrrolidinone (NVP) b) polyvinylpyrrolidone (PVP) c) Sodium Dodecyl Sulfate (SDS) and d) polyethylenimine (PEI)

Adsorption studies were conducted on RDX to understand how each dispersant adsorbs to the RDX particles. In the adsorption study, the selected energetic material was placed in a solution of deionized water and dispersant (2 mg/ml) in which the pH level was carefully controlled. Different amounts of dispersant were used to make different weight percent solutions and the zeta potential of the particles were measured. Adsorption studies were conducted for PVP and PEI on RDX. The results from the study are plotted in Figure 7 and Figure 8. In the adsorption study, different amounts of PVP (wt% with respect to the solution) were placed in water and the pH level was lowered by adding nitric acid and raised by adding ammonium hydroxide to the solution. The zeta potential of the particles was then measured and the results are shown in Figure 7. Effective PVP adsorption was confirmed when the particles had the zeta potential closest to zero as PVP does not have a charge in water. When the particles are covered with polymer, steric effects from the polymer prevent them from coming close enough to agglomerate permanently. It is clear that as little 0.1 wt% PVP solutions is the most practical for the RESS-AS process as adequate adsorption of PVP occurs onto RDX at this weight percent. Therefore, only small amounts of PVP will be needed with RESS-AS tests. From Figure 7, it is clear that in acidic suspensions PVP has almost no net charge (zero zeta potential). However, at high pH level suspensions and at low weight percentages PVP does provide more electrostatic dispersion. Therefore, it is reasonable to conclude that PVP coated particles will flocculate together in low pH-level suspensions but should be dispersible in higher pH-level suspensions.

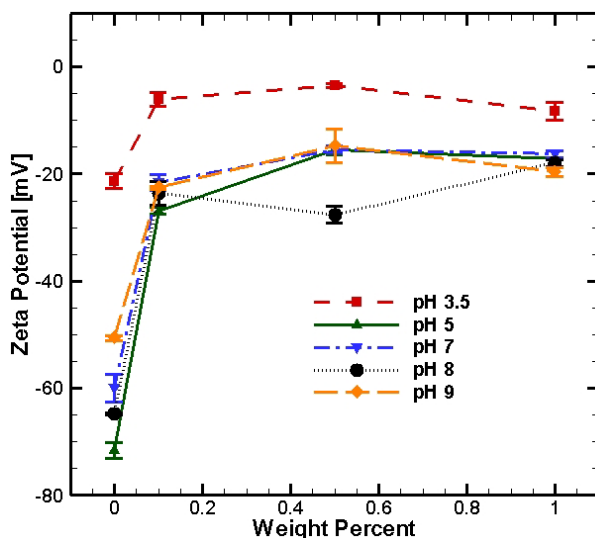


Figure 7. PVP adsorption study on RDX

Slightly different results were seen with the adsorption study for PEI onto RDX. It can be seen that with zero weight percent polymer the zeta potential of the RDX ranged from -20 to -70 mV depending on the pH level of the solution. This was seen with the PVP study as well. However, once a small amount of PEI was added, the zeta potential became positive from the cationic nature of PEI in water. This implies that as little as 0.1 wt% PEI in solution is more than enough to provide adequate dispersion for the RDX particles. It is also apparent that a pH level of around 8 will provide the most electrostatic dispersion at low weight percents and a pH level outside of this value will provide a zeta potential closer to zero providing less electrostatic dispersion. The added cationic electrostatic dispersion is also very helpful as well as for keeping particles from agglomerating.

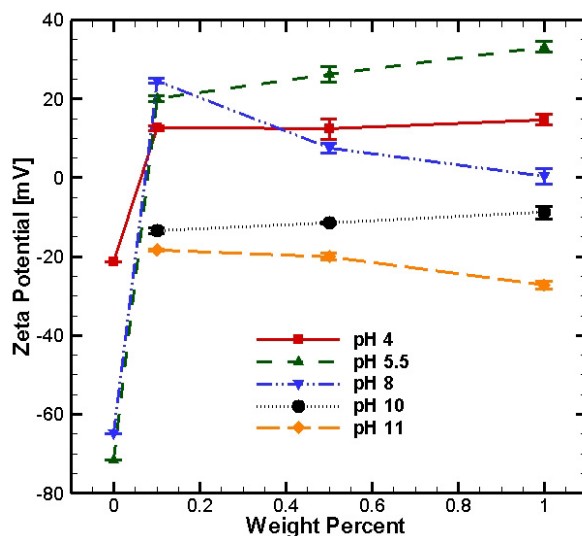


Figure 8. PEI adsorption study on RDX

PARTICLE ANALYSIS

Two methods were used to determine the size of the produced particles. The first method was image analysis and the second method was dynamic light scattering (DLS). For image analysis of the particles, a JEOL 6700F FE-SEM was used to take images of the collected particles. A few drops of a colloidal suspension (RESS-AS samples) or some of the dry powder (RESS samples) made from the tests were placed on carbon tape atop an aluminum stub. The samples were then vacuum dried to

remove the water and other volatile materials while leaving the particles behind. Each sample was iridium coated to help to reduce charge build up on the sample for imaging purposes. Images from the entire sample were taken so that measurements would not have a bias towards a specific particle size. Following this, FE-SEM images were imported into image analysis software (Image J; National Institute of Health). The images were converted into a binary image and the area of the particles were calculated by the software. After the areas were taken, they were converted into particle diameters. A suitable number of measurements had to be taken to make sure that the sampling error was as low as possible.²¹ This was to serve as a comparison to DLS measurements and to provide important information about the particle's morphology. In addition to image analysis, particle size characteristics were analyzed while the particles were in their colloidal suspensions by DLS. DLS measurements were taken with a Brookhaven ZetaPALS instrument. The recorded particle size was based on a volume percentage. Size distributions were then created from this information.

The particle's zeta potential was determined in water for each individual test. Finding the zeta potential allowed one to understand particle stability in a suspension. Stabilization of particulate materials is critical to processing high quality and exceptionally dense parts. Critical parameters to understand are the sedimentation and flocculation behaviors of a suspension as well as the conditions that lead to agglomeration. A well dispersed suspension should produce particles which can be tightly packed with few packing defects.

THERMAL ANALYSIS OF PRODUCED PARTICLES

Some early research by Stepanov *et al.*¹³ with RDX produced from the RESS process investigated the melting point of RDX produced from this process. They found that the melting temperature for their produced particles in the range from 100-200 nm was the same as micron-sized RDX. This finding also agrees with the authors' results for 100 nm sized particles. In order to determine any alterations of thermal properties based upon the particle's size range, a smaller particle sizes down to 10s of nm is required. Knowing that a single RDX molecule can be approximated to be around 0.6 nm in diameter²², the percentage of mass on the surface of a 100 nm particle is approximately 3%. It is known that when the percentage of molecules on the surface of a particle becomes a non-negligible percentage of the mass of a particle, the particle's thermal properties can then change significantly. Two of these effects are lower melting temperatures and heat capacities, but another is a higher internal energy of the particle. The higher internal energy comes from shorter bond lengths of molecules at a particle's surface. The conversion of these higher energy bonds into their normal combustion products could produce more propulsive or explosive energy than the bulk-sized energetic materials with equivalent mass. Smaller particles (with 10s nm in diameter produced from the RESS-AS process) would be advantageous for investigation, since these particles could have a large percentage of their mass on the surface of the particle. The internal energy of a single nano-sized particle can be expressed as the sum of two parts by the following expression:

$$E = NE^0 + A_s E^s \quad (2)$$

where E represents the internal energy of the particle with known volume, E^0 is the bulk internal energy per molecule, N the number of molecules, E^s the surface internal energy per unit area, and A_s the surface area of the particle. From this expression, it can be seen that nanoparticles can store extra energy in comparison to bulk materials due to their higher percentage of molecules on the particle's surface. In view of second term associated with the surface energy, nano-sized particles could provide a possibility to store greater internal energy than bulk-sized particles. Therefore, solid propellants and/or explosives containing these nano-sized particles with high percentages of surface molecules can be more energetic than those containing equal weight percentages of micron-sized particles.

For these reasons, some preliminary thermal analysis was performed on the RESS and RESS-AS synthesized particles. The produced particles were analyzed with a Netzsch simultaneous thermal analyzer (STA) 449F1. The device is both a DSC and TGA. Approximately 5 mg samples were placed in

alumina (Al_2O_3) crucibles with a vented lid. The samples were placed in a He environment with a flow rate of 20.0 ml/min and with a heating rate of 10.0 K/min. Military grade RDX, RESS synthesized RDX (Test 001), and RESS-AS synthesized RDX (Test 002; neat water solution) were all analyzed and compared.

RESULTS AND DISCUSSION

RESULTS FOR RESS PRODUCES PARTICLES

FE-SEM images of the produced RDX particles from the RESS process with a pre-expansion pressure of 34.5 MPa and pre-expansion temperature of $T_0=85^\circ\text{C}$ can be seen in Figure 9. Primary particles were approximately 100 nm in diameter and often larger. The particles were also aggregated and agglomerated together. This was confirmed by DLS measurements in which a 100 nm peak was seen along with a 500 nm peak (Figure 10). This agrees well with the results from image analysis. Particles possessed a round and smooth shape. While particles were fairly uniform in shape, there were particles with different shapes and sizes than others. This probably is a result of coagulation during the expansion process. This observation is interesting as supercritical fluid precipitation is expected to have high and uniform degrees of supersaturation, forming very uniform particles. The observed agglomeration is usually seen with other researchers as there is not a method present to stabilize the particles during and after the supercritical solution expansion. Therefore, agglomerated and aggregated particles are commonly found. The results clearly show that fine particles can be precipitated, but stabilization and prevention of coagulation could improve the qualities of the particles by an even larger amount by making them smaller and more dispersed.

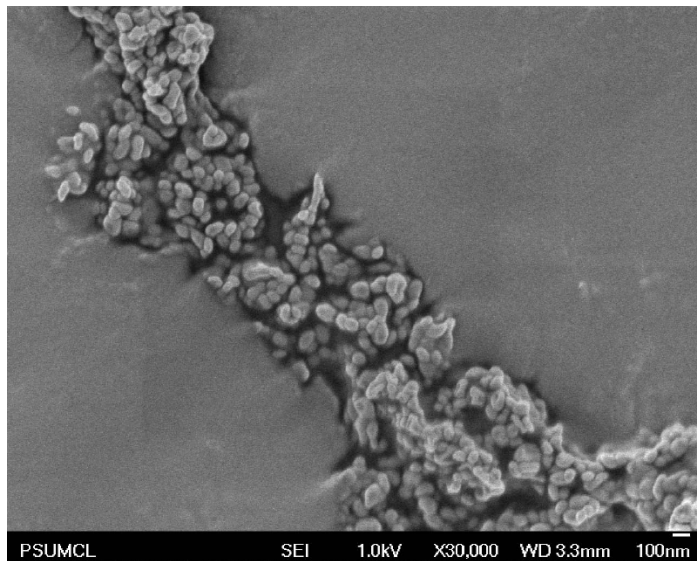


Figure 9. RDX particles produced from RESS process (Test 001; $P_0=34.5$ MPa, $T_0=85^\circ\text{C}$)

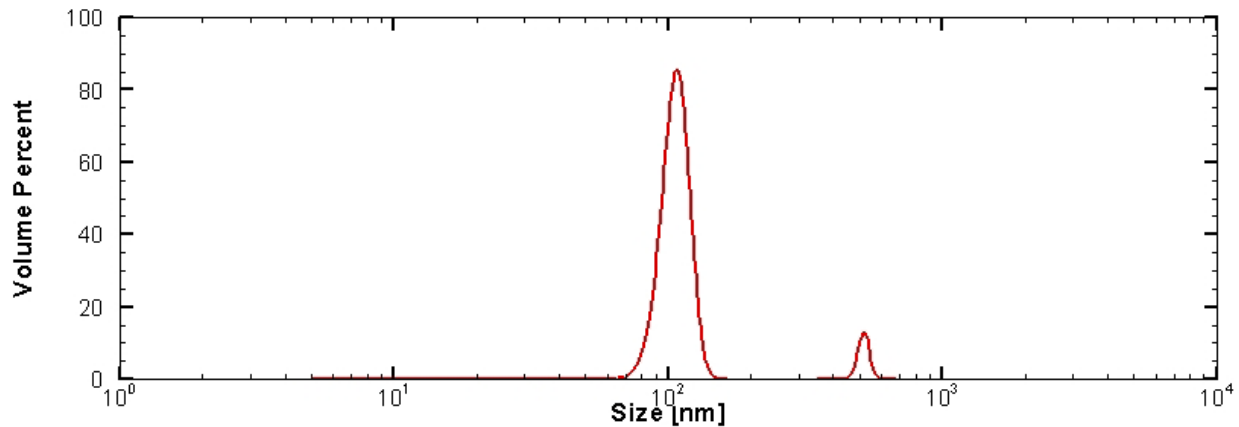


Figure 10. RDX particle size distribution from RESS testing (Test 001)

RESS results for BTAT were encouraging. Synthesized particles were rounder and significantly smaller than the as-received particles. FE-SEM images of these particles can be seen in Figure 11. The primary particles appear to be slightly greater than 100 nm. However, many of these particles were bridged and agglomerated in an even worse manner than the RDX. This suggests that during early particle nucleation and growth the precipitated particles were all individual particles and proceeded to grow as individual particles. Processes after the initial nucleation and growth such as coagulation and agglomeration probably caused the undesirable traits in the final product. Changing the expansion environment could alleviate some of these complications and could adequately separate the particles.

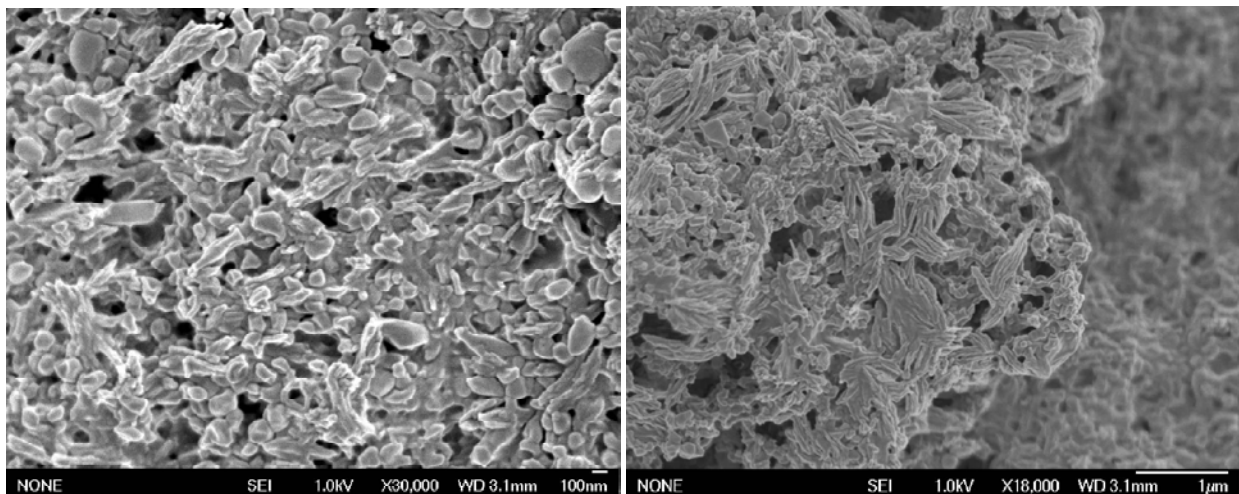


Figure 11 FE-SEM Image of RESS Synthesized BTAT Particles (Test 008)

RESULTS FOR RESS-AS PRODUCED PARTICLES

Clear differences in the size and dispersion of particles produced from the RESS-AS process were observed in comparison to the RESS process. One of the first tests conducted involved a supercritical solution of RDX expanded into neat water. Particles with a diameter around 30 nm were produced through this method. FE-SEM images of the produced particles can be seen in Figure 12. Image analysis results found an average particle size of approximately 34 nm. DLS analysis of the particles showed that almost no agglomeration occurred initially and the median particle size was 30 nm (Figure 13) and agreed well with the results from image analysis. It is immediately clear that the produced particles are significantly smaller in size than RESS synthesized RDX. The RESS-AS produced particles tended to have a more spherical shape than RDX particles produced through the RESS process.

The fact that particles could be so well dispersed and have a smaller size is encouraging for future processing applications. The different results from the expansion into neat water can be explained by the fact that RDX was shown to have a fairly strong zeta potential (-30 mV) in suspension after a test. Therefore, water does have a stabilizing influence on the particles when they are produced in neat water as an electrostatic force prevents the particles from growing larger by aggregation from coagulation. It is clear that in order to produce small nano-sized particles of RDX through supercritical fluid precipitation, it is necessary to have a properly designed post expansion environment that can quench the growth of the particles.

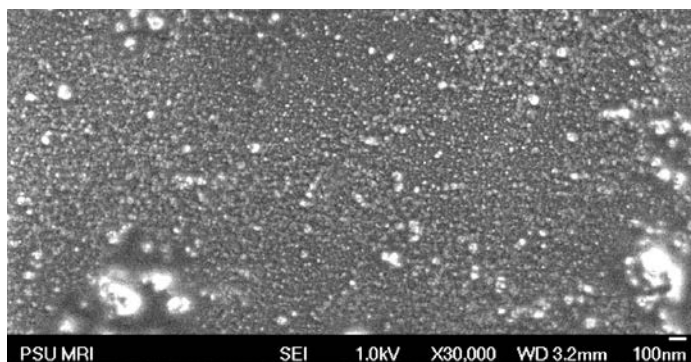


Figure 12. RDX Particles from RESS-AS into neat water (Test 002, $T_0=353$ K, $P_0=34.5$ MPa) at 30,000x magnification

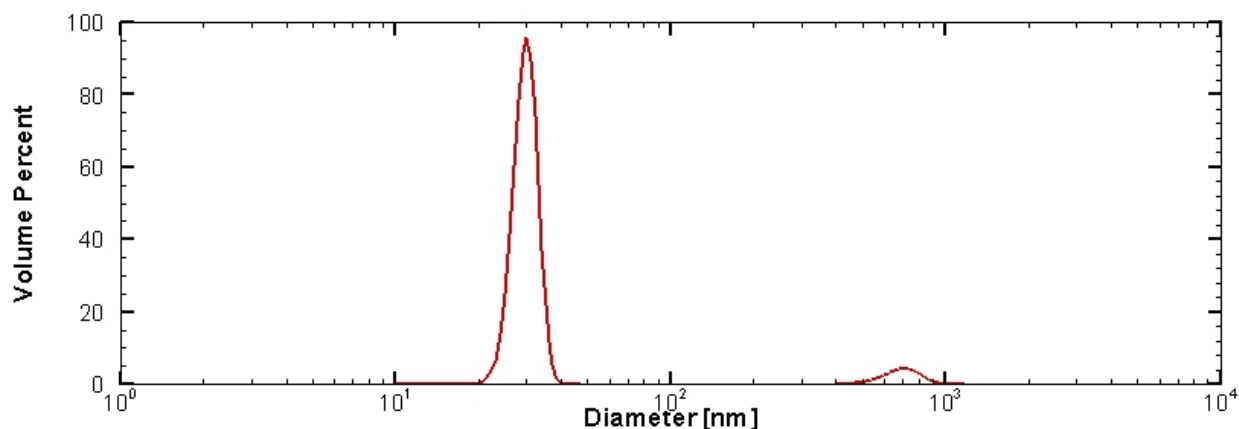


Figure 13. Particle size distribution for RDX and supercritical CO₂ solution expanded into neat water (Test 002)

NVP was the first dispersant to be used with the RESS-AS process. NVP is known to have an affinity to negatively charged surfaces. Adsorption of this polymer could potentially prevent permanent agglomeration of the particles. Figure 14 displays the DLS size distribution results of nano-sized RDX particles synthesized by RESS-AS tests using NVP as the dispersing agent. From the size distribution results it can be seen that there are two peaks of 37 nm and one of about a micrometer. This small size is comparable to what was produced from expanding into neat water (Test 002). The extra size increase of the primary particles in comparison to Test 002 is probably from the adsorbed polymer. The second peak at a size of one micrometer is from agglomerated particles resulting in the drop of zeta potential of the particles from the adsorbed polymer (-10 mV), which would suggest that van der Waals forces are stronger than electrostatic dispersion forces in the suspension.

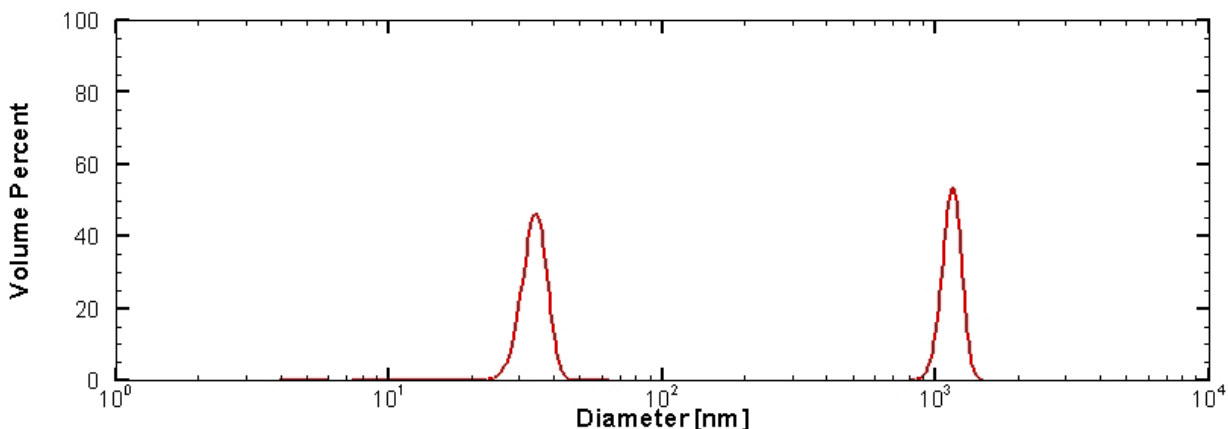


Figure 14. Particle size distribution of RDX particles synthesized by the RESS-AS process from expansion into water/NVP solution (Test 003)

In addition to the results from expanding the supercritical solutions into neat water, expansion into PVP solutions showed a good deal of promise. The first test (Test 004) used (0.1 wt%) PVP and the second test (Test 005) used 0.005 wt% PVP. The DLS size distribution results are shown in Figure 15. Test 005 produced slightly smaller particles than Test 004. The DLS results display large agglomerates which were clear upon visual inspection of the suspension. After a test, the collected suspension was noticeably cloudy. The particles tended to flocculate together after a test allowing them to be collected by sedimentation. Once collected, if the pH level of the water was changed to a value of 8.0 or higher the PVP coated particles dispersed into numerous small particles with some limited agglomerates. Evidence of this pH level induced dispersion is clearly seen in Figure 16. However, the particles could not be reduced to a size less than around 60 nm. This is probably because of the high molecular weight of the PVP used. This shows that as little as 0.005 wt% is needed to adequately coat the particles. This is a sharp contrast to NVP, in which the particles could not be redispersed. This suggests that the steric hindrance provided by the polymer prevented the particles from permanently agglomerating. Therefore, it is reasonable to suspect that the DLS did not measure the actual particle size but the size of the agglomerates which could subsequently be redispersed after a test. With some more careful fine tuning, the size of the final particles could be altered to be even smaller while the particles are sterically protected from agglomeration. This could be achieved by using a lower molecular weight PVP polymer to reduce the coating size on the particles. The sedimentation behavior could also be helpful in separating the useful energetic material from the solution. Once separated from solution, the particles could then be redispersed to mix with fuel or cast into a solid part.

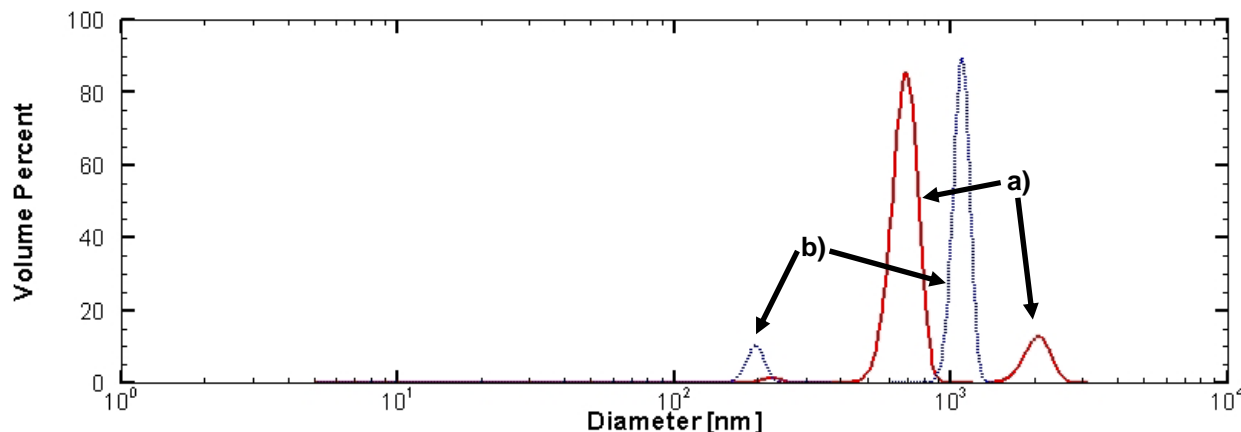


Figure 15. Size distributions of RESS-AS produced particles expanded into water/PVP solution (a) Test 004 solid red line with higher percent of PVP, b) Test 005 dotted blue line with lower percent of PVP

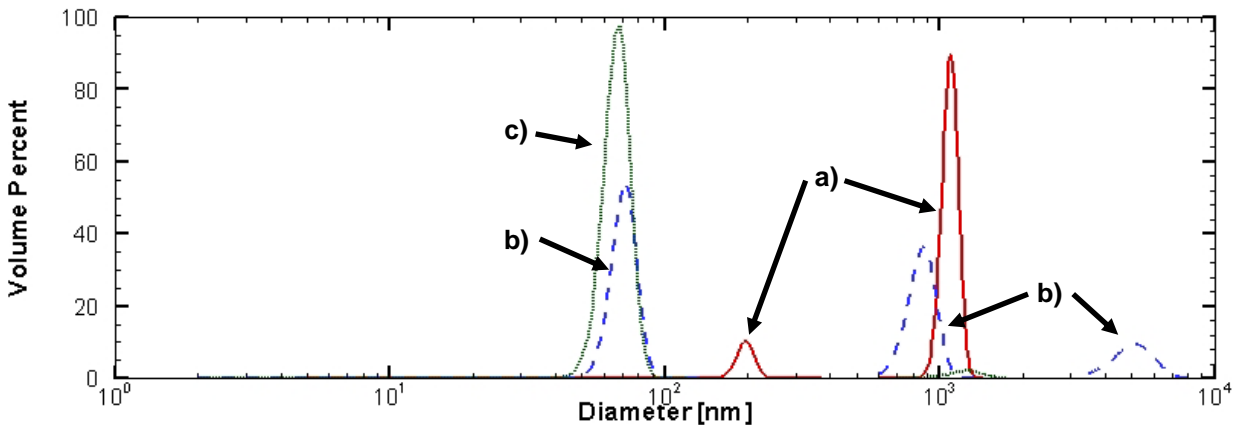


Figure 16. The effect of pH level on particle size distributions for Test 005 a) pH 5 solid line, b) pH 7 dashed line, c) pH 11 dotted line)

The polymer PEI also showed encouraging results when used with the RESS-AS process. The DLS size results for these tests can be seen in Figure 17. The initial test (0.05 wt %) produced agglomerated particles that could not be redispersed. These agglomerates had a median size of 5 micrometers. However, lowering the weight percent (0.005 wt%) produced smaller particles that could be redispersed by altering the pH level of the solution. PEI would also flocculate and sediment out as PVP suspensions did, but the particles would redisperse even easier than PVP coated particles. In addition to steric protection, the polymer increased the zeta potential of the suspended particles to around 20.0 mV which allowed for some electrostatic dispersion as well. Therefore, it can be seen that only trace amounts of PEI are needed to adequately disperse RDX particles in water. It is also interesting to note that by altering the suspension pH level from 5 to 7 dramatically disperses the particles as shown in Figure 18. This makes sense as this is the pH level that provided the highest zeta potential in the adsorption study. As with the case with PVP, particles can be collected by sedimentation. With the PEI coating, the particles should be protected against permanent agglomeration for a much longer period of time than Test 002, which just has electrostatic dispersion. Also, PEI has a lower molecular weight than PVP and therefore the coated primary particles are significantly smaller than PVP coated particles (37 nm vs. 60 nm). This shows that PEI can be a very advantageous dispersing agent.

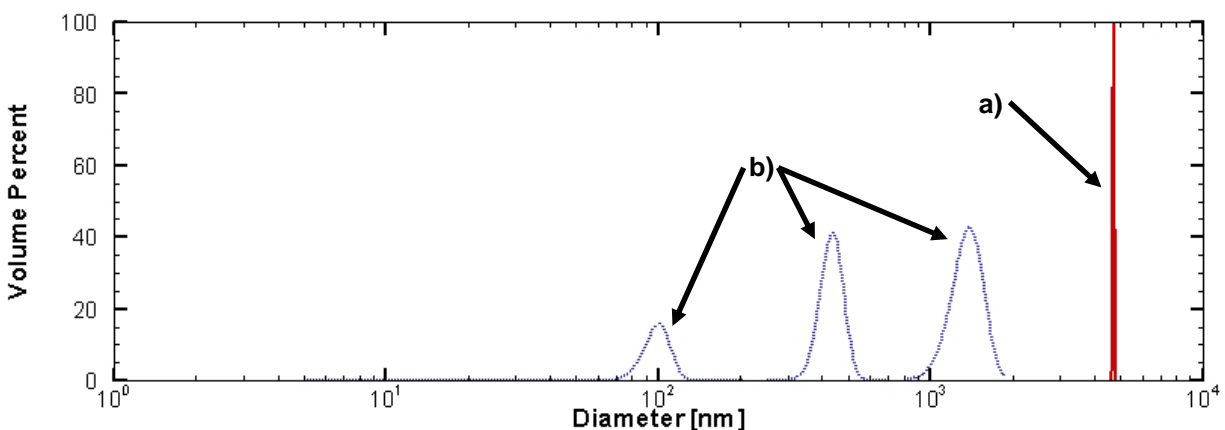
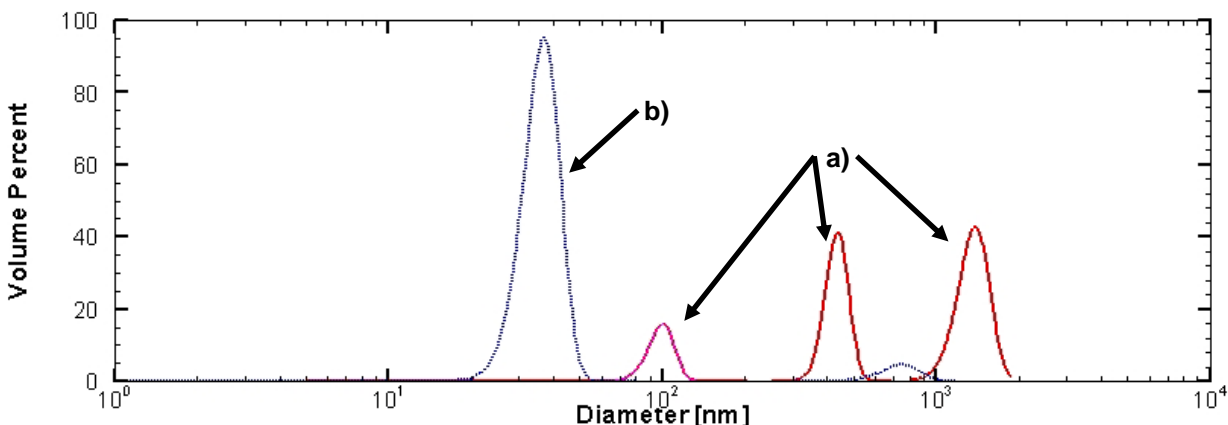


Figure 17. Particle size distribution of RESS-AS test expanded into water/PEI solution a) Test 006 solid red line with higher percentage of PEI, and b) Test 007 dotted blue line with lower percentage of PEI



**Figure 18. The effect of pH level on particle size distributions for Test 007 using water/PEI solution
a) pH 5 solid line, b) pH 7 dotted line**

In addition to RDX, BTAT particles were synthesized with the RESS-AS process. Initial tests involved the precipitation of BTAT into neat water (Test 009). However, the particles that were created were agglomerated masses. It was decided that heavy flocculation occurs during the precipitation process and a dispersing agent would be needed to make individual particles.

BTAT was also expanded into a solution of SDS and water. The final particles had a very unique shape. The produced particles tended to form square like rods that were about 1-2 micrometers in length with an aspect ratio of around 5. The produced particles can be seen in Figure 19. The current explanation for this particular shape is that SDS surfactant could have the tendency to form admicelles in water which would promote the development of crystals with high aspect ratios.¹⁷ The fact that the surfactant was able to change the shape of the final particles suggests that crystal growth is still occurring in the aqueous solution. The shape of these particles would not be as ideal as spherical particles, but it is still an improvement over the original plate-like particles. Further research is needed to form more desirable spherical particles.

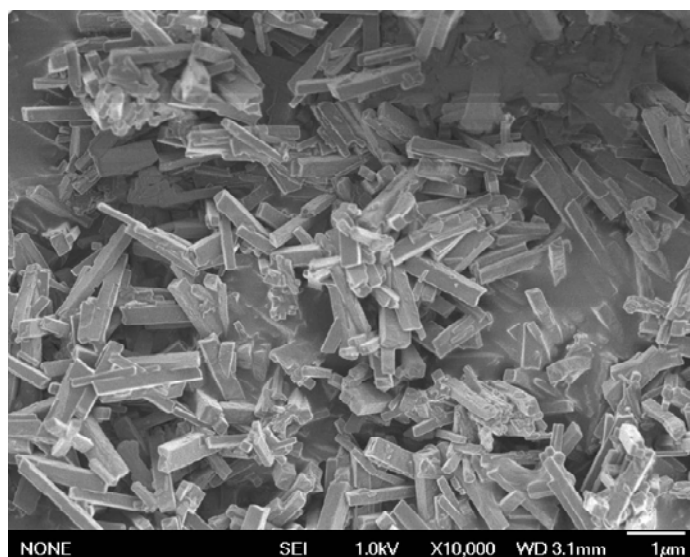


Figure 19. BTAT particles produced from RESS-AS process using water/SDS solution (Test 010)

THERMAL BEHAVIOR OF PRODUCED PARTICLES

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on the produced particles. Military grade RDX (Figure 3), RESS synthesized RDX (Figure 9), and RESS-AS synthesized RDX (Figure 12) were all analyzed for comparison purposes. The DSC curves for these three types of RDX can be seen in Figure 20. There are noticeable differences between the curves. It is interesting to note that the RESS synthesized RDX did not experience a noticeable shift in melting or decomposition temperature from military RDX. The results indicate that even the small size of RESS synthesized RDX (~100 nm) is not small enough to cause any noticeable changes in the thermodynamic properties of the material. This is reasonable because 100 nm particles would only have approximately 3% of their mass on their surface.

Of greater interest is the shift in endothermic and exothermic behavior of the RDX nano-sized particles produced from the RESS-AS process (Test 003). The 25° C shift in the exothermic peak temperature is fairly significant and similar results have been recorded by some other researchers.⁷ This is meaningful in that RDX particles produced from the RESS-AS process have enough mass on their surface (~12 %) to see a shift in thermal behavior while the particles produced from the RESS process do not show these trends. This implies that the RESS-AS process produces particles small enough to have altered thermodynamic and reactive properties. More work in quantifying the energy of these particles should yield valuable information on how the smaller size of these particles can change the specific heat, internal energy, and activation energy of the energetic material at this size scale. These smaller particles could be more energetic if used in propellants and explosives due to the ability of nano-sized particles to store energy on their surfaces. However, their lower decomposition temperatures could make them more sensitive to initiation as well, so the pros and cons should be carefully weighed. It would be interesting to see how sensitive these particles are, because the particles should have less defects but they also will decompose at a lower temperature. Clearly, more research is needed to investigate this important behavior.

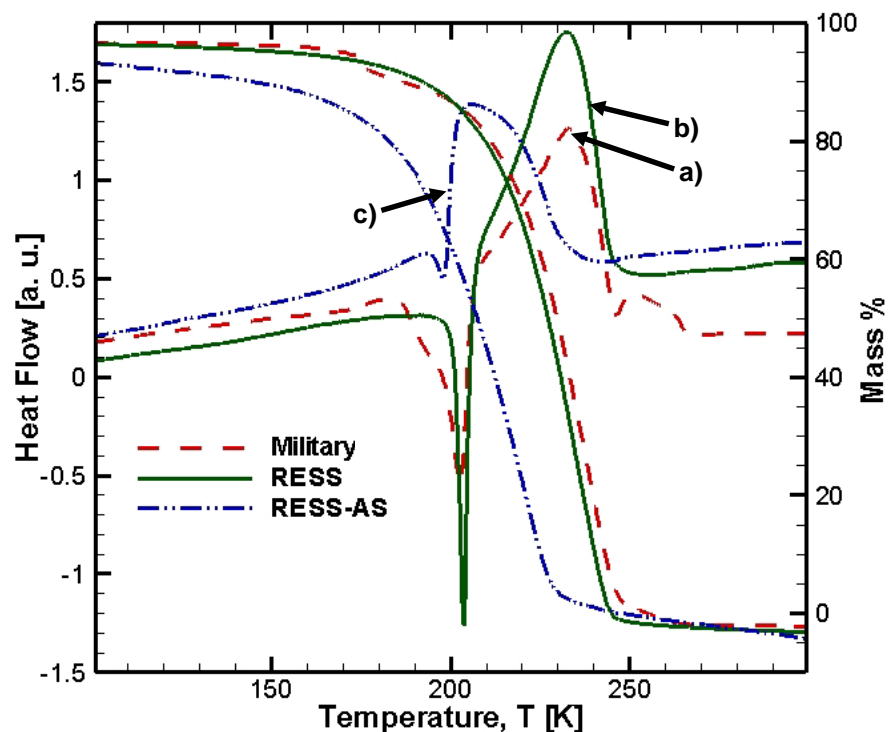


Figure 20. DSC and TGA curves of a) military grade RDX (dashed red curve), b) RESS synthesized RDX (solid green curve), and c) RESS-AS synthesized RDX (dot-dash blue curve)

CONCLUSION

Particles of RDX and BTAT were synthesized with the RESS and RESS-AS processes. RDX was synthesized using the RESS process to obtain 100 nm particles with noticeable larger agglomerates. In contrast, the RESS-AS process was used to create RDX nanoparticles significantly smaller (~30 nm) than RDX particles precipitated from the RESS process. RDX precipitated into neat water was shown to be relatively stable. Two dispersants (PVP and PEI) were shown to be effective in coating RDX particles in solution. Particles synthesized with both of these polymers showed initial agglomeration from the reduction in the absolute value of the particle's zeta potential in suspension, but this was reversible by changing the pH level of the solution which subsequently dispersed the particles. The reversibility of the particle agglomeration in these tests suggests that both of these polymers provided sufficient coating to prevent permanent agglomeration. The coating thickness was found to be extremely thin for PEI. This makes PEI a more attractive choice as a dispersant in comparison to PVP. The production of these nano-RDX particles could have several key benefits. They could be less sensitive, have more energy release, and burn faster than conventional RDX. Early thermal analysis indicates that the particles produced from the RESS-AS process experience a temperature shift in their endothermic and exothermic behavior. With a significant amount of mass at their surface, it is expected that other thermal properties such as internal energy are altered as well. The RESS process has been proven control the morphology and size distributions of BTAT particles. Preliminary study of BTAT particles produced from the RESS process showed that small round-shaped particles can be produced (~100 nm), but these particles were heavily aggregated together without using any dispersants. BTAT particles were also synthesized with the RESS-AS process. It was found that when expanded into a water/SDS solution, small nano-sized rods with a square-shaped cross-sectional area were synthesized. Using other dispersants, round-shaped particles of BTAT is possible to achieve. These small nano-sized energetic particles should be less sensitive to impact. More characterization studies will be necessary in the future to realize the full potential of these particles.

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